

# PATENT COOPERATION TREATY

## PCT

REC'D 03 APR 2002

WIPO PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/KR 00/01039	International filing date (day/month/year) 15 September 2000 (15.09.2000)	Priority Date (day/month/year) 15 September 1999 (15.09.1999)
International Patent Classification (IPC) or national classification and IPC  IPC <sup>7</sup> : C08G 75/14; C08L 95/00		
Applicant SHIM Kyung Sup		

1.	This international preliminary examination report has been prepared by this International Preliminary Examination Authority and is transmitted to the applicant according to Article 36.
2.	This REPORT consists of a total of <u>  3  </u> sheets, including this cover sheet.  <input type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  These annexes consist of a total of _____ sheets.
3.	This report contains indications relating to the following items: <ul style="list-style-type: none"> <li>I.      <input checked="" type="checkbox"/> Basis of the opinion</li> <li>II.     <input type="checkbox"/> Priority</li> <li>III.    <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV.    <input type="checkbox"/> Lack of unity of invention</li> <li>V.     <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability: citations and explanations supporting such statement</li> <li>VI.    <input type="checkbox"/> Certain documents cited</li> <li>VII.   <input type="checkbox"/> Certain defects in the international application</li> <li>VIII. <input type="checkbox"/> Certain observations on the international application</li> </ul>

Date of submission of the demand  <div style="text-align: center;">12.04.2001</div>	Date of completion of this report  <div style="text-align: center;">13 December 2001 (13.12.2001)</div>
Name and mailing address of the IPEA/AT Austrian Patent Office Kohlmarkt 8-10 A-1014 Vienna Facsimile No. 1/53424/200	Authorized officer  <div style="text-align: center;">BÖHM</div> Telephone No. 1/53424/519

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/KR 00/01039

**I. Basis of the report**1. With regard to the **elements** of the international application:\*☒ the international application as originally filed☐ the description:

pages \_\_\_\_\_ as originally filed

pages \_\_\_\_\_ filed with the demand

pages \_\_\_\_\_ filed with the letter of \_\_\_\_\_

☐ the claims:

pages \_\_\_\_\_ as originally filed

pages \_\_\_\_\_ as amended (together with any statement) under Article 19

pages \_\_\_\_\_ filed with the demand

pages \_\_\_\_\_ filed with the letter of \_\_\_\_\_

☐ the drawings:

pages \_\_\_\_\_ as originally filed

pages \_\_\_\_\_ filed with the demand

pages \_\_\_\_\_ filed with the letter of \_\_\_\_\_

☐ the sequence listing part of the description:

pages \_\_\_\_\_ as originally filed

pages \_\_\_\_\_ filed with the demand

pages \_\_\_\_\_ filed with the letter of \_\_\_\_\_

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).☐ the language of publication of the international application (under Rule 48.3(b)).☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:☐ contained in the international application in printed form.☐ filed together with the international application in computer readable form.☐ furnished subsequently to this Authority in written form.☐ furnished subsequently to this Authority in computer readable form.☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.4. ☐ The amendments have resulted in the cancellation of:☐ the description, pages \_\_\_\_\_☐ the claims, Nos. \_\_\_\_\_☐ the drawings, sheets/fig \_\_\_\_\_5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as „originally filed“ and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/KR 00/01039

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement	Novelty (N)	Claims 3-11	YES
		Claims 1,2,12	NO
Inventive step (IS)		Claims 3-11	YES
		Claims 1,2,12	NO
Industrial applicability (IA)		Claims 1-12	YES
		Claims	NO

### Citations and explanations (Rule 70.7)

The following documents have been cited in the Search Report:

D1: JP 10 081680 A  
D2: GB 1121305 A  
D3: DE 2016568 A

The subject matters of claims 1, 2, and 12 cannot be considered to be novel and to involve an inventive step, because some of the substances, which are expressed by the formula (I) are those polyphenol sulphides of the of the formulas (I) or (II) of the JP 10 081680.

So the molecular weights are the same too.

The compound of formula (II) of the JP10081680 is useful as a photoenergy-converting material, like claim12 of the present invention proposes.

The subject matters of claims 3-11 can be considered novel and to involve an inventive step, because none of the publications cited in the search report discloses the features as characterized in claims 3-11, which are not obvious for a person skilled in the art.

Industrial applicability of all claims is given.

## INTERNATIONAL SEARCH REPORT

International Classification No.  
PCT/KR 00/01039

## CLASSIFICATION OF SUBJECT MATTER

IPC<sup>7</sup>: C08G 75/14; C08L 95/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>7</sup>: C08G; C08L; C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AT, Chem. Abstracts

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO: WPI, PAJ, STN: CAS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 10 081680 A (COS MO) 31 March 1998 (31.03.98) (abstract). [online] [retrieved on 1998-06-30]. Retrieved from: EPOQUE PAJ Database.	1-2,12
X	GB 1121305 A (DUNLOP COMPANY) 24 July 1968 (24.07.68) claims.	3-5
A	DE 2016568 A (SOCIÉTÉ NATIONALE DES PÉTROLES D'AQUITAINE) 15 October 1970 (15.10.70) claims.	6-10

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

„A“ document defining the general state of the art which is not considered to be of particular relevance  
„E“ earlier application or patent but published on or after the international filing date  
„L“ document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
„O“ document referring to an oral disclosure, use, exhibition or other means  
„P“ document published prior to the international filing date but later than the priority date claimed

„T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
„X“ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
„Y“ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  
„&“ document member of the same patent family

Date of the actual completion of the international search  
12 December 2000 (12.12.2000)Date of mailing of the international search report  
23 February 2001 (23.02.2001)Name and mailing address of the ISA/AT  
Austrian Patent Office  
Kohlmarkt 8-10; A-1014 Vienna  
Facsimile No. 1/53424/535Authorized officer  
BÖHM  
Telephone No. 1/53424/519

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.  
PCT/KR 00/01039

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
DE	C2	2016568	15-04-1982	BE	A1	748638	16-09-1970
DE	A	2016568	15-10-1970	FR	A5	2036843	31-12-1970
				GB	A	1303318	17-01-1973
				NL	A	7004949	13-10-1970
				NL	B	166966	15-05-1981
				NL	C	166966	15-10-1981
GB	A	1121305		none			
JP	A2	10081680	31-03-1998	none			

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
 US Department of Commerce  
 United States Patent and Trademark  
 Office, PCT  
 2011 South Clark Place Room  
 CP2/5C24  
 Arlington, VA 22202  
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 06 June 2001 (06.06.01)	
<b>International application No.</b> PCT/KR00/01039	<b>Applicant's or agent's file reference</b>
<b>International filing date (day/month/year)</b> 15 September 2000 (15.09.00)	<b>Priority date (day/month/year)</b> 15 September 1999 (15.09.99)
<b>Applicant</b> SHIM, Kyung, Sup	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

12 April 2001 (12.04.01)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland	<b>Authorized officer</b>  Zakaria EL KHODARY
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 March 2001 (22.03.2001)

PCT

(10) International Publication Number  
WO 01/19724 A2

(51) International Patent Classification<sup>7</sup>: C01B  
(21) International Application Number: PCT/KR00/01039  
(22) International Filing Date:  
15 September 2000 (15.09.2000)  
(25) Filing Language: English  
(26) Publication Language: English  
(30) Priority Data:  
1999/39522 15 September 1999 (15.09.1999) KR

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant and  
(72) Inventor: SHIM, Kyung, Sup [KR/KR]; Hyundai Apartment 205-1202, Apgujung-dong, Kangnam-ku, Seoul 135-110 (KR).

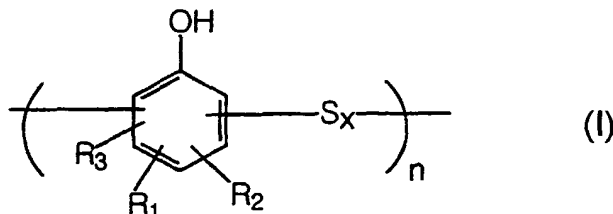
**Published:**

— Without international search report and to be republished upon receipt of that report.

(74) Agent: CHOI, Hong, Soon; Markpro Patent & Law Firm, KFSB Building, 8th floor, 16-2, Yeodo-dong, Yeongdeungpo-ku, Seoul 150-110 (KR).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A NOVEL AROMATIC POLYSULFIDE AND AN ASPHALT COMPOSITION CONTAINING THE SAME



(57) Abstract: The present invention relates to a novel aromatic polysulfide and an asphalt composition containing the same, and more particularly, to a novel aromatic polysulfide having repeating units of formula (I), an asphalt composition, an asphalt paving composition, an adhesion promoter and an UV absorber containing the same. The asphalt paving composition of this invention exhibits excellent adhesiveness to aggregate component and better water resistance, and renders the temperature susceptibility less sensitive, thereby greatly improving durability.

**A NOVEL AROMATIC POLYSULFIDE AND AN ASPHALT  
COMPOSITION CONTAINING THE SAME**

**5 BACKGROUND OF THE INVENTION**

**Field of the Invention**

The present invention relates to a novel aromatic polysulfide and an asphalt composition containing the same. More particularly, this invention relates to a novel aromatic polysulfide and an asphalt composition, an adhesive  
10 promoter and an ultraviolet absorber containing the same.

**Description of the Related Art**

Korean Patent Application No. 1993-14434 discloses a modified asphalt composition comprising 0.5-100 wt% of polyolefin-type metal complex based  
15 on the 100 wt% of asphalt in order to improve physical properties of prior asphalt composition.

Korean Patent Application No. 1996-81058 reports a novel asphalt modifier with lower viscosity and odor-free character and an asphalt composition containing the above asphalt modifier, prepared in such a manner that  
20 naphthenic acid containing sulfur compound and other impurities is separated by distillation at the temperature of 70-200°C and then remaining volatile portions are removed by passing inert gas, after which oils such as lubricating oil are added to the treated compound. Korean Patent Application No. 1992-8279 also sets forth a cold-mixed asphalt paving composition containing  
25 straight asphalt, gas oil and polymeric hardening agent.

Meanwhile, U.S. Patent Nos. 4,244,747, 4,234,346 and 4,801,332 disclose an improved asphalt composition further comprising organic metal compound

such as organic manganese compound, organic cobalt compound. Furthermore, U.S. Patent No. 4,008,095 describes an asphalt paving composition comprising microgranular undigested coal particles, bituminous coal and asphalt.

5 An asphalt composition comprising polyolefins modified with a carboxyl group and/or other functional group derived from the carboxyl group is described in Japanese Patent Kokai Nos. Sho 54-139925, Sho 59-138263, Sho 60-158256, Sho 62-181358 and Sho 62-275160.

U.S. Patent No. 5,710,196 provides an asphalt composition comprising a  
10 graft copolymer, for example, acrylonitrile-butadiene-styrene copolymer resin so as to enhance the properties of asphalt composition. Furthermore, in order to reduce the cracking of asphalt, especially at low temperatures due to heavy loads, U.S. Patent Nos. 4,547,399, 4,835,199 and 5,002,987 suggest compositions of elastomeric copolymers and asphalt.

15 However, the conventional asphalt compositions including the aforementioned compositions fail to meet the requirement for excellent asphalt, for example, adhesiveness, water resistance, cracking-durability and abrasion resistance.

In the meantime, copolymer of metacrylic ester mono and vinyl monomer,  
20 which has the chromophore group representing different ultraviolet (hereinafter referred to as "UV") absorption patterns from the metacrylic ester mono is provided as an UV absorber in Korean Patent Application No. 1988-700951. In addition, Korean Patent Application No. 1995-3408 discloses a novel bezazol compound designed for the UV absorber, prepared in such a manner  
25 that carboxylic derivatives and o-phenyldiamine are reacted at the temperatures ranging between 20°C-90°C in the presence of chloro sulfonic acid.

In an effort to reduce the detrimental effect of UV by absorbing UV, Korean Patent Application No. 1989-18583 provides conjugated bis-1,3-diketone derivatives of benzene and Korean Patent Application No. 1989-19891 provides a composition comprising oligomer of cyclohexenilidene cyanoacetate.

5

## SUMMARY OF THE INVENTION

To solve the long-felt need in the art, the inventor has made intensive studies and as a result, developed a novel aromatic polysulfide polymer, noting that the aromatic polysulfide polymer may improve various properties of asphalt composition and serve as excellent an UV absorber.

10

Accordingly, an object of this invention is to provide a novel aromatic polysulfide polymer and a method for preparing the same.

Another object of this invention is to provide an asphalt composition comprising the above polysulfide.

15

Still another object of this invention is to provide an adhesion promoter applied to polymer resin and an UV absorber.

Other objects and advantages of this invention will become more apparent from the detailed description to follow taken in conjunction with the appended claims.

20

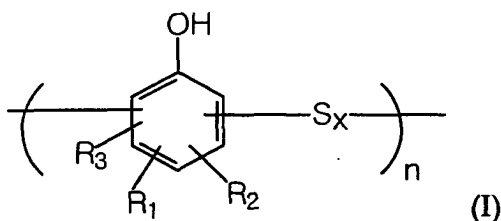
## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph representing the UV transmission pattern of the present polysulfide.

25

## DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a novel aromatic polysulfide having repeating units of the following formula (I):



5            wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same or different from each other, and independently represent H, unsubstituted alkyl group, substituted alkyl group, unsubstituted aryl group or substituted aryl group;  $x$  is an integer of 1-4; and  $n$  is an integer of 2-10,000.

10            The structural feature of the present aromatic polysulfide is that elements in the 6B group, oxygen and sulfur, which have two electron lone pairs, are bonded to benzene nucleus. The electron lone pairs of oxygen and sulfur can simultaneously interact with cations, which may be components of asphalt paving composition, through electrostatic interaction, thereby improving a variety of physical properties of an asphalt paving composition.

15            The benzene ring of the polysulfide provides an ability to serve as excellent an UV absorber.

20            The average molecular weight of the present polysulfide may vary depending on polymerization, but preferably in the range of 5,000 to 20,000, and more preferably in the range of 7,000 to 15,000. If the molecular weight of the polysulfide is less than 5,000, an asphalt composition and an asphalt paving composition containing such polymer may be worse in view of durability, though inducing better processability. If the molecular weight is more than 20,000, the processability may be decreased, though temperature susceptibility and durability are increased.

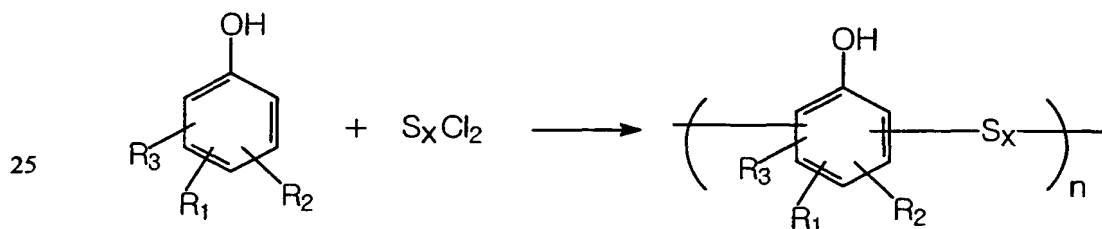
25            The substituents in the aromatic polysulfide of this invention may be any substituents, but preferably including unsubstituted alkyl group, substituted alkyl group, unsubstituted aryl group or substituted aryl group.

As used herein, "alkyl" means a branched or unbranched saturated hydrocarbon chain, which can be unsubstituted or substituted. For example, C<sub>1</sub>-C<sub>6</sub> straight or branched alkyl hydrocarbon chain contains 1 to 6 carbon atoms, and includes but is not limited to substituents such as methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, tert-butyl, n-pentyl, n-hexyl, and the like, unless otherwise indicated. The substituted alkyl has substituent(s) at one or more positions selected from halo, nitro, hydroxyl, alkyl, alkeyl, alkoxy, alkenyloxy, phenoxy, benzyloxy or aryl.

The term "aryl", alone or in combination, is defined herein as a monocyclic or polycyclic group, preferably a monocyclic or bicyclic group, i.e. phenyl or naphthyl, which can be unsubstituted or substituted, for example, with one or more and, in particular, one to three substituents selected from halogen, alkyl, hydroxy, alkoxy, haloalkyl, nitro, amino, acylamino, alkylthio, alkylsulfinyl and alkylsulfonyl. Some exemplary aryl groups include phenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2-methylphenyl, 4-methoxyphenyl, 3-trifluoromethylphenyl, 4-mitrophenyl, and the like.

This invention also relates to a method for preparing a novel aromatic polysulfide represented by the following scheme (I), comprising the step of reaction between phenol analogue and sulfur chloride species:

Scheme (I)



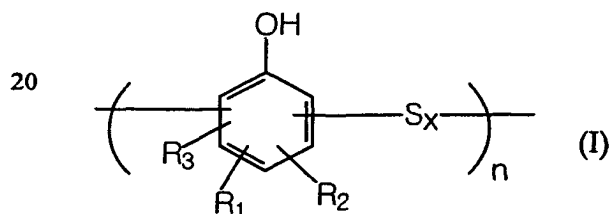
wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same or different from each other, and

independently represent H, unsubstituted alkyl group, substituted alkyl group, unsubstituted aryl group or substituted aryl group; x is an integer of 1-4; and n is an integer of 2-10,000.

As explained above, the method of the present invention is performed by the reaction of phenol or phenol derivatives and sulfur chloride species, which may be classified as condensation polymerization, and the reaction condition is mild. For instance, the preferred reaction temperature is in the range of 50°C-90°C.

In addition, it is preferred that the method of this invention further comprises the step of adding an alkyl halide or aryl halide so as to add various substituents into the benzene nucleus. According to the method of this invention, the sulfur chloride species used is selected from the group consisting of sulfur dichloride, sulfur monochloride, trisulfur dichloride and tetrasulfur dichloride, and the most preferred sulfur chloride species is sulfur monochloride.

This invention provides an asphalt composition comprising: (i) a novel aromatic polysulfide having repeating units of the following formula (I):



wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same or different from each other, and independently represent H, unsubstituted alkyl group, substituted alkyl group, unsubstituted aryl group or substituted aryl group; x is an integer of 1-4; and n is an integer of 2-10,000; and (ii) an asphalt.

The aromatic polysulfide contained in the asphalt composition is

responsible for improving various properties such as penetration, ductility, and temperature susceptibility. According to the preferred example, the amount of the polysulfide compound is from 0.5 to 10 wt% and the amount of the asphalt is from 90 to 99.5 wt% based on the weight of the composition. If  
5 the amount of the polysulfide is less than 0.5 wt%, the effect of adding polysulfide may be negligible, but in case of exceeding 10 wt%, cracking is caused by hardening of the composition. Furthermore, if the amount of asphalt composition is less than 90 wt%, the fluidity may be decreased, but in excess of 99.5 wt%, the durability may be dramatically decreased though strength is  
10 increased.

This invention also relates to an asphalt paving composition comprising an asphalt composition aforementioned (comprising 0.5 to 10 wt% of polysulfide having repeating units of formula (I) and 90 to 99.5 wt% of asphalt), aggregate,  
15 stone powder and sand. According to the preferred example, the asphalt paving composition comprises 4 to 10 wt% of the asphalt composition, 65 to 85 wt% of the aggregate, 3 to 10 wt% of the stone powder and 8 to 25 wt% of the sand.

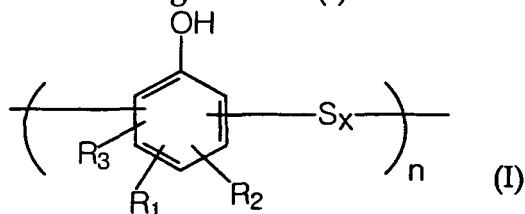
According to this invention, an useful asphalt can be any conventional  
20 asphalt in the art, and preferably includes straight asphalt, blown asphalt, lake asphalt, rock asphalt, sand asphalt, asphaltite, etc., and the most preferably includes straight asphalt.

In the asphalt paving composition of this invention, if the amount of the asphalt composition is less than 4 wt%, the physical strength and the fluidity  
25 may be remarkably decreased, but in case of exceeding 10 wt%, the durability may be decreased.

The asphalt paving composition exhibits excellent adhesiveness to

aggregate component and better water resistance, and renders the temperature susceptibility less sensitive, thereby greatly improving durability.

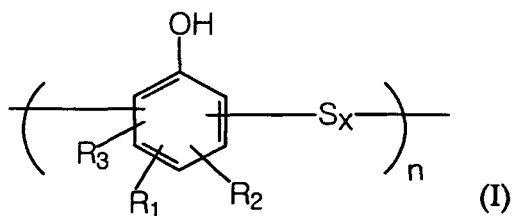
This invention also provides an adhesion promoter applied to polymer resin, which comprises a novel aromatic polysulfide having repeating units of the following formula (I):



wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are the same or different from each other, and independently represent H, unsubstituted alkyl group, substituted alkyl group, unsubstituted aryl group or substituted aryl group;  $x$  is an integer of 1-4; and  $n$  is an integer of 2-10,000.

The aromatic polysulfide serving as an adhesion promoter renders polymer resin (for example, polyethylene, polypropylene, polyisobutylene, polyvinylchloride, polystyrene, polyvinylacetate, polyisoprene) containing the polysulfide to be more adhesive.

This invention provides an UV absorber comprising a novel aromatic polysulfide having repeating units of the following formula (I):



wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are the same or different from each other, and independently represent H, unsubstituted alkyl group, substituted alkyl group,

unsubstituted aryl group or substituted aryl group; x is an integer of 1-4; and n is an integer of 2-10,000.

The aromatic polysulfide may function as an UV absorber in paint, plastic film, etc. to reduce sensitivity to UV, thereby extending the life span of such product.

The following specific examples are intended to be illustrative of the invention and should not be construed as limiting the scope of the invention as defined by the appended claims.

10

#### **EXAMPLE 1 : Preparation of the Aromatic Polysulfide of this Invention I**

In a 5-necked flask of 5 liters fitted with 2-additional funnels, water cooled condenser, agitator and thermometer was placed *para*-cresol (2160 g: 20 mole) and heated to 70°C . To it was added sulfur monochloride (2835 g: 21mole) dropwise while maintaining the reaction temperature at 50°C-70°C . When 70% of the sulfur monochloride was added, methylene chloride (1000 ml) was introduced. Then, the remaining sulfur monochloride was added, and heated for an additional hour at 70°C-80°C .

Upon completion of the reaction, 2000 ml of water was added to remove any unreacted sulfur monochloride. Removal of solvent and water gave a dark yellowish solid polymer.

The resultant polymer shows about 8,000 of the average molecular weight and 80°C of the melting point. The IR absorption spectrum of the polymer exhibits troughs at 3400 cm<sup>-1</sup> , 1440 cm<sup>-1</sup> , 1220 cm<sup>-1</sup> and 1160 cm<sup>-1</sup>.

25

#### **EXAMPLE 2 : Preparation of the Aromatic Polysulfide of this Invention II**

The aromatic polysulfide according to this invention was prepared in the

same manner as in EXAMPLE 1, except that phenol was used instead of *para*-cresol.

The final product shows about 8,000 of the average molecular weight and 80°C of the melting point.

5

**EXAMPLE 3 : Preparation of the Aromatic Polysulfide of this Invention III**

The aromatic polysulfide according to this invention was prepared in the same manner as in EXAMPLE 1, except that *meta*-cresol was used instead of *para*-cresol.

10 The yielded product shows about 8,000 of the average molecular weight and 80°C of the melting point.

**EXAMPLE 4 : Preparation of the Aromatic Polysulfide of this Invention IV**

15 The aromatic polysulfide according to this invention was prepared in the same manner as in EXAMPLE 1, except that mixed cresol (including *ortho*-cresol, *para*-cresol and *meta*-cresol) was used instead of *para*-cresol.

The yielded product shows about 8,000 of the average molecular weight and 80°C of the melting point.

20 **EXAMPLE 5 : Preparation of the Asphalt Composition of this Invention**

1 wt%, 2 wt% and 3 wt% of aromatic polysulfide prepared in EXAMPLE 1 were respectively added to 99 wt%, 98 wt% and 97 wt% of straight asphalt, thereby making total weight percent of the final composition 100 wt%. Then while melting, each mixture was completely mixed to yield the asphalt  
25 composition at 150°C .

**EXAMPLE 6 : Preparation of the Asphalt Paving Composition of this Invention**

6 wt% of each asphalt composition prepared in EXAMPLE 5, 34 wt% of aggregate having 19-13 mm of particle size, 40 wt% of aggregate having less than 13 mm of particle size, 15 wt% of sand and 5 wt% of stone powder were heated and mixed to yield the asphalt paving composition at 150°C .

**EXPERIMENTAL EXAMPLE 1 : Evaluation on Properties of the Asphalt Composition of this Invention**

The various physical properties (including penetration, ductility, softening temperature and index of temperature susceptibility) of the asphalt composition prepared in EXAMPLE 5 were evaluated based on KS M 2252, KS M 2254 and KS M 2250, respectively. The results are summarized below Table 1:

**EXPERIMENTAL EXAMPLE 2 : Evaluation on Properties of the Asphalt Paving Composition of this Invention**

The Marshall test on asphalt paving composition prepared in EXAMPLE 6 was carried out based on KS F 2337. And the Wheel tracking test on the asphalt paving composition prepared in EXAMPLE 6 was performed so as to evaluate resistance to rutting caused by wheels based on the Manual for Testing Qualities of Construction issued by the Korea Highway Corporation. The results are summarized below in Table 1:

TABLE 1

Items	Physical Properties		Amount of aromatic polysulfide(wt%)		
			1	2	3
Asphalt Composition	Penetration (1/10mm, 25℃)		85	82	79
	Ductility (cm, 25℃)		150	150	150
	Index of temperature susceptibility (℃)		0.0263	0.0178	0.0161
	Softening temp.(℃)		59	67	72
Asphalt Paving Composition	Marshall test	Stability(kg)	1.687	1.892	1.956
		Fluidity(1/100cm)	30	28	27
		Porosity(%)	4.02	4.51	4.78
	Wheel tracking	Ratio of deformation(mm/min)	0.035	0.014	0.009
		Dynamic stability(times/mm)	921	1237	1516

### EXPERIMENTAL EXAMPLE 3 : Evaluation on the Enhancing Adhesion of the Aromatic Polysulfide of this Invention

In order to evaluate the adhesion enhancement of the polysulfide, 3 wt% of the polysulfide prepared in EXAMPLE 1 were added to the PVC solution in THF (tetrahydrofuran), the resultant was then coated on a stainless steel plate and finally dried. Following the lapse of proper time, the extent of adhesion was observed with the naked eyes. It was noted that the PVC solution containing the polysulfide of this invention adhered strongly to the stainless steel plate, thus not observing peeling off, but the PVC solution without the polysulfide was peeled off from the plate with a lapse of time.

As a result, it is confirmed that the polysulfide of this invention may remarkably enhance the adhesion of polymer resin.

**EXPERIMENTAL EXAMPLE 4 : Evaluation on the UV Transmittance of the  
Aromatic Polysulfide of this Invention**

In an effort to evaluate the UV transmittance of the polysulfide prepared in EXAMPLE 1, 0.016 g of the polysulfide was dissolved in 8 ml of chloroform solution and then the UV transmittance was measured with UV-spectrophotometer (HP-8454). The transmittance was calculated in the following equation and the result was plotted as shown in Fig. 1:

**Equation (I)**

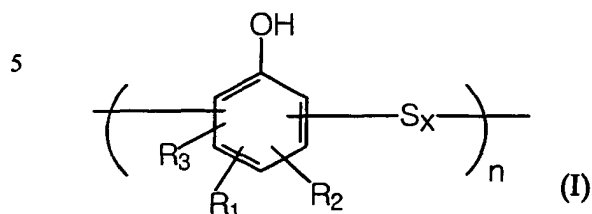
$$\text{Transmittance (T)} = 10^{-A(\lambda)}$$

wherein  $A(\lambda)$  is absorbance.

As shown in Fig. 1, the polysulfide of this invention represents a much lower transmittance in the UV region and therefore has excellent property as an UV absorber.

What is claimed is:

1. A novel aromatic polysulfide having repeating units of the following formula (I):

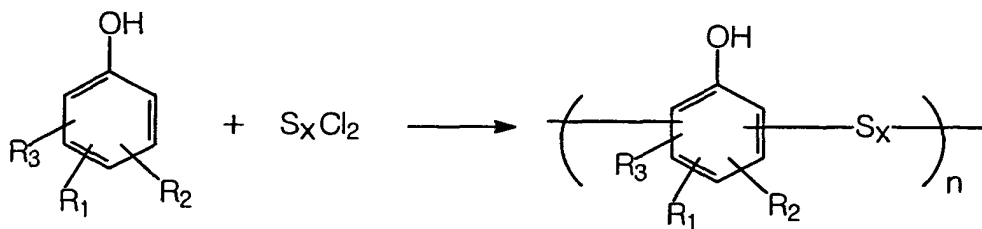


wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same or different from each other, and  
 10 independently represent H, unsubstituted alkyl group, substituted alkyl group,  
 unsubstituted aryl group or substituted aryl group;  $x$  is an integer of 1-4; and  $n$   
 is an integer of 2-10,000.

2. The novel aromatic polysulfide according to claim 1, wherein the average  
 15 molecular weight of the aromatic polysulfide is from 5,000 to 20,000.

3. A method for preparing a novel aromatic polysulfide represented by the  
 following scheme (I), comprising the step of reaction between phenol or  
 derivatives thereof and sulfur chloride species:

20 **Scheme (I)**



25

wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same or different from each other, and  
 independently represent H, unsubstituted alkyl group, substituted alkyl group,

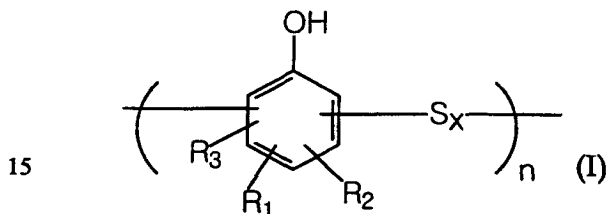
unsubstituted aryl group or substituted aryl group; x is an integer of 1-4; and n is an integer of 2-10,000.

4. The method according to claim 3, wherein the sulfur chloride species is sulfur monochloride.

5. The method according to claim 3, wherein the method further comprises the step of adding an alkyl halide or aryl halide.

6. An asphalt composition, which comprises

(i) a novel aromatic polysulfide having repeating units of the following formula (I):



wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same or different from each other, and independently represent H, unsubstituted alkyl group, substituted alkyl group, unsubstituted aryl group or substituted aryl group; x is an integer of 1-4; and n is an integer of 2-10,000; and

(ii) an asphalt.

7. The asphalt composition according to claim 6, wherein the amount of the polysulfide compound is from 0.5 to 10 wt% and the amount of the asphalt is from 90 to 99.5 wt% based on the weight of the composition.

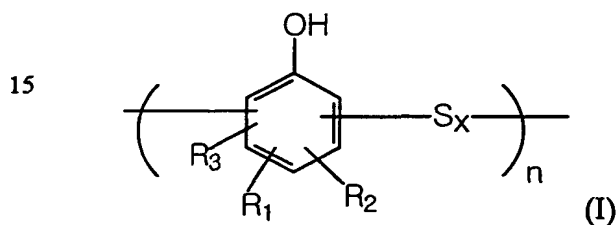
8. The asphalt composition according to claim 6 or 7, wherein the asphalt is

selected from the group consisting of straight asphalt, blown asphalt, lake asphalt, rock asphalt, sand asphalt and asphaltite.

9. An asphalt paving composition comprising the asphalt composition of claim  
5 6, aggregate, stone powder and sand.

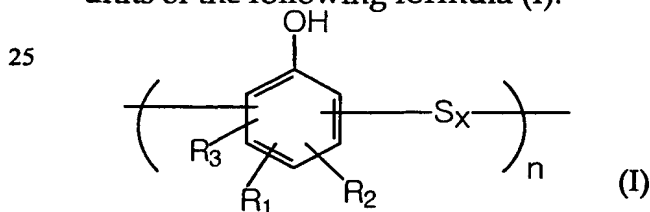
10. The asphalt paving composition according to claim 9, wherein the amount  
of the asphalt composition is from 4 to 10 wt%, the amount of the aggregate is  
from 65 to 85 wt%, the amount of the stone powder is from 3 to 10 wt% and the  
10 amount of the sand is from 8 to 25 wt%.

11. An adhesion promoter applied to polymer resin, which comprises a novel  
aromatic polysulfide having repeating units of the following formula (I):



wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same or different from each other, and  
independently represent H, unsubstituted alkyl group, substituted alkyl group,  
20 unsubstituted aryl group or substituted aryl group;  $x$  is an integer of 1-4; and  $n$   
is an integer of 2-10,000.

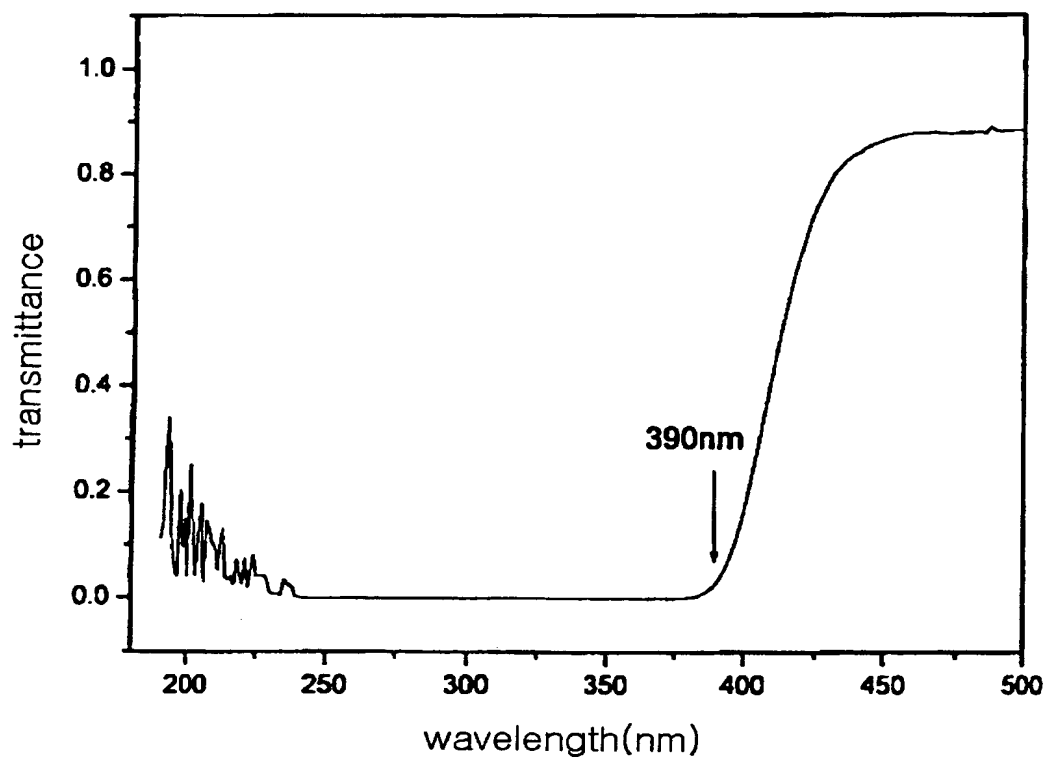
12. An UV absorber comprising a novel aromatic polysulfide having repeating  
units of the following formula (I):



wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same or different from each other, and independently represent H, unsubstituted alkyl group, substituted alkyl group, unsubstituted aryl group or substituted aryl group;  $x$  is an integer of 1-4; and  $n$  is an integer of 2-10,000.

1/1  
**FIGURE**

**Fig. 1**



(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 March 2001 (22.03.2001)

PCT

(10) International Publication Number  
**WO 01/19724 A3**

(51) International Patent Classification<sup>7</sup>: C08G 75/14,  
C08L 95/00

(21) International Application Number: PCT/KR00/01039

(22) International Filing Date:  
15 September 2000 (15.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
1999/39522 15 September 1999 (15.09.1999) KR

(71) Applicant and

(72) Inventor: SHIM, Kyung, Sup [KR/KR]; Hyundai Apartment 205-1202, Apgujung-dong, Kangnam-ku, Seoul 135-110 (KR).

(74) Agent: CHOI, Hong, Soon; Markpro Patent & Law Firm, KFSB Building, 8th floor, 16-2, Yeodo-dong, Yeongdeungpo-ku, Seoul 150-110 (KR).

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

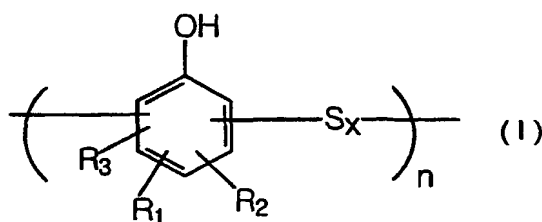
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:  
— with international search report

(88) Date of publication of the international search report:  
2 August 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A NOVEL AROMATIC POLYSULFIDE AND AN ASPHALT COMPOSITION CONTAINING THE SAME



(57) Abstract: The present invention relates to a novel aromatic polysulfide and an asphalt composition containing the same, and more particularly, to a novel aromatic polysulfide having repeating units of formula (I), an asphalt composition, an asphalt paving composition, an adhesion promoter and an UV absorber containing the same. The asphalt paving composition of this invention exhibits excellent adhesiveness to aggregate component and better water resistance, and renders the temperature susceptibility less sensitive, thereby greatly improving durability.